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**NOTE**

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# Etching characteristics of bismuth single crystals in aqueous nitric acid

K C Poria
Crystal Growth Laboratory, Department of Physics,
South Gujarat University, Surat-395 007, India

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**Abstract** : The results of etching the (111) planes of bismuth single crystals in aqueous solutions of fuming nitric acid are reported. For the compositions studied, triangular etch-pits are produced at the sites of dislocations of the (111) $[10\bar{1}]$ type. The activation energies for the lateral motion of ledges within the etch-pits have been obtained. No change in etch-pits morphology has been observed either with a change in composition or temperature of the etchants.

**Keywords** : Bismuth single crystals, etch-pits, activation energy

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The simple but useful technique of etching can be applied to study the reactivity at dislocations. This technique has been exploited to a large extent to reveal dislocations in metals, semiconductor and organic and inorganic molecular solids only. There does not seem to exist much work in the literature to use this technique to study the reactivity at dislocations. As part of an extensive programme to study the reactivity at dislocations in metals and organic molecular solids, the present work was undertaken.

The crystals used in this investigation were grown by the horizontal zone-levelling technique from bismuth metal of 5N purity obtained from Nuclear Complex, Hyderabad, India. The crystals were grown with a 0.5 cm zone movement at 1 cm/hr.

The crystals were cleaved in the conventional manner at liquid nitrogen temperatures by keeping the edge of a sharp blade parallel to the (111) face and striking a gental blow on it. The freshly cleaved surfaces were rinsed in ether and hot-air dried.

The etchants were made from analar grade fuming nitric acid to which doubly distilled water was added. Three etchant compositions were used; (A) equal parts of fuming

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nitric acid and distilled water, (B) 4 parts of fuming nitric acid and 6 parts of water and (C) 3 parts of fuming nitric acid and 7 parts of water. The etching times increased with increase in water content and the samples were etched at different temperatures upto 65°C.

All the three etchants produced well defined triangular, crystallographically oriented etch-pits on etching for periods of 3 secs to 10 secs. Figure 1 is a photomicrograph depicting the type of etch-pits produced. These etchants were fested to confirm that they revealed dislocations. These dislocations were of the (111) [10$\bar{1}$] type. The etch-pits size increased with temperature; the increase being linear. Figure 2 shows a typical plot of the etch-pits size increase with temperature. The etch-pit sizes were measured using a micrometer eyepiece on a Carl Zeiss $NU_2$ Universal Research Microscope.

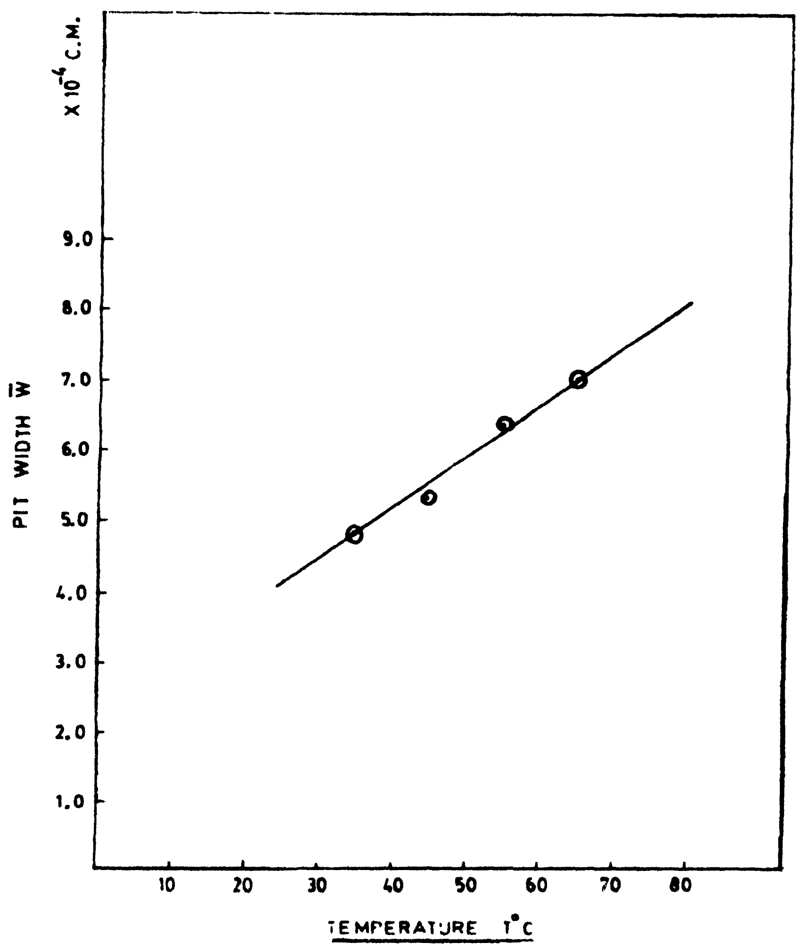


**Figure 2.** Plot of etch pit size *versus* temperature.

The activation energies were measured using the Arhenius law :

$$W = A \exp(-E/RT),$$

***Plate I***

**Figure 1.** Photomicrograph showing the type of etch pits produced on etching (111) cleavage plane of bismuth.

where $W$ is the width of the pit and $T$ is the absolute temperature. Figure 3 is a typical plot of low $W$ *vs* $1/T$ for one of the etchants studied. The activation energies for the lateral

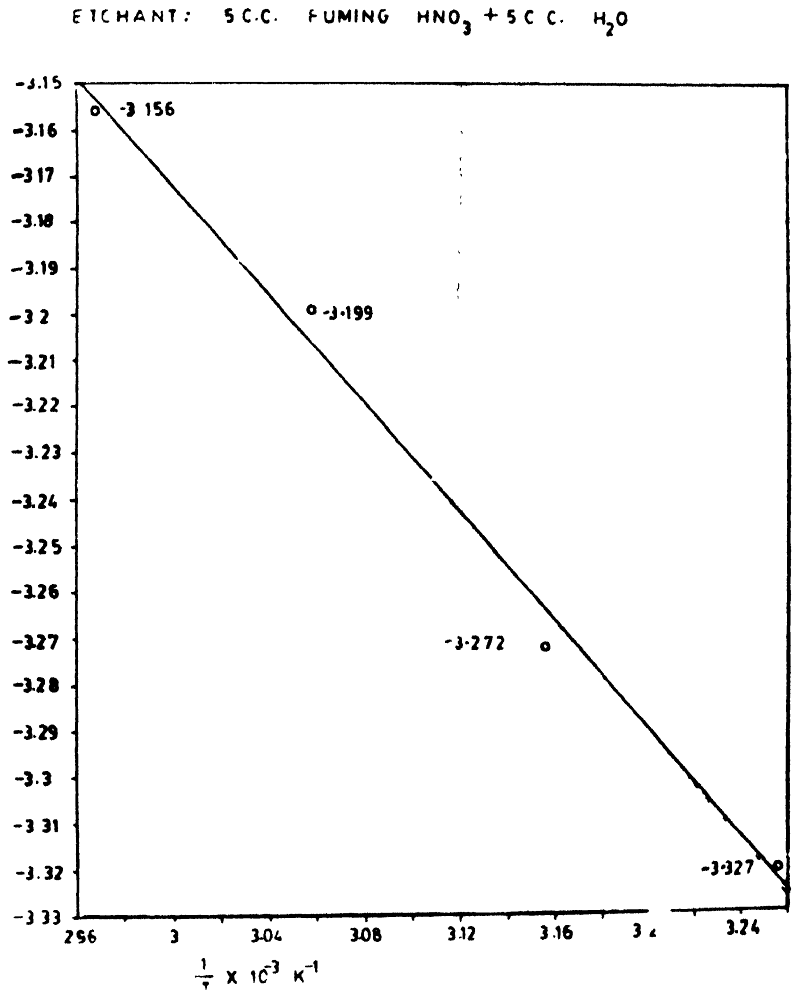


**Figure 3.** Plot of low $W$ *versus* $1/T$ for etchant (a).

motion of edges at the dislocations were 0.13 eV, 0.18 eV and 0.06 eV for the three etchants (a), (b) and (c) respectively. Table 1 summarizes these results.

**Table 1.** Activation energies of the etchants

| Sr. No. | Etchants | Activation energy eV |
|---|---|---|
| | 5 C.C. Fuming $HNO_3$ + 5 C.C. Distilled $H_2O$ | 0.13 eV |
| | 4 C.C. Fuming $HNO_3$ + 6 C.C. Distilled $H_2O$ | 0.18 eV |
| 3. | 3 C.C. Fuming $HNO_3$ + 7 C.C. Distilled $H_2O$ | 0.06 eV |

The structure of bismuth is rhombohedral with $a = 4.74$ Å and $\alpha = 57.23$. The physical properties are highly anisotropic and far from what one might expect from an almost cubic structure. The atoms in a-layer perpendicular to the triangular axis are held by covalent bonds and these in turn are held by Van der Waals forces [1].

Bismuth being nearly cubic, the mode of deformation by slip is similar to the face centered cubic metals and the dislocations revealed by the present etchant are of the (111) $[10\bar{1}]$ type as observed from their alignments on the cleavage surface.

The activation energies for the tangential motion of steps at the dislocation etch-pits exhibit a non-linear behaviour with increase in water content. This type of behaviour has also been observed in nitric acid and ethyl alcohol etchants diluted with various amounts of water [2,4,5]. This change which is occurring at a fixed composition may be due to change in kink kinetics taking place in the ledges on account of changes in the oxidation state of bismuth [3,6].

The etchants reveal dislocations of the (111) $[10\bar{1}]$ type. The non-linear behaviour of the activation energies for the lateral motion of ledges at dislocations is due to changes in kink kinetics on account of changes in the oxidation state of bismuth.

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